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ATTORNEY'S DOCKET NUMBER
60843

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**

U.S. APPLICATION NO. (if known, see 37 C.F.R. 1.5)

10/018536

INTERNATIONAL APPLICATION NO.
PCT/DE0001775

INTERNATIONAL FILING DATE
31 May 2000

PRIORITY DATE CLAIMED
02 July 1999

TITLE OF INVENTION
**CATALYST COMPOSITION AND PROCEDURE FOR THE MANUFACTURE OF SYNDIOTACTIC STYRENE
POLYMERS**

APPLICANT(S) FOR DO/EO/US
Jurgen Schellenberg

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor (35 U.S.C. 371(c)(4)).
10. ☐ A translation of the Annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 15. below concern other document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ A FIRST preliminary amendment.
☐ A SECOND or SUBSEQUENT preliminary amendment.
13. ☐ A substitute specification.
14. ☐ A change of power of attorney and/or address letter.
15. ☐ Other items or information:

U.S. APPLICATION NO. (If known, see 37 C.F.R. 1.50) 10/018536	INTERNATIONAL APPLICATION NO. PCT/DE0001775	ATTORNEY'S DOCKET NUMBER 60843
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17. ☒ The following fees are submitted:

Basic National Fee (37 CFR 1.492(a)(1)-(5)):

Search Report has been prepared by the EPO or JPO	\$	890.00
International preliminary examination fee paid to USPTO (37 CFR 1.482)	\$	710.00
No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2))	\$	740.00
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445 (a)(2)) paid to USPTO	\$	1,040.00
International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4)	\$	100.00

ENTER APPROPRIATE BASIC FEE AMOUNT =

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Surcharge of \$ **130.00** for furnishing the oath or declaration later than ☐ 20 ☒ 30 months from the earliest claimed priority date (37 CFR 1.492(e)).

\$ **130.00**

Claims	Number Filed	Number Extra	Rate
Total Claim	20 - 20 =	0	X \$ 18.00
Independent Claims	2 - 3 =	0	X \$ 84.00
Multiple dependent claim(s) (if applicable)			\$ 0.00

\$ **0.00**

\$ **0.00**

\$ **0.00**

Processing fee of \$ **0** for furnishing the English Translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(f)).

\$ **0.00**

TOTAL NATIONAL FEE =

\$ **1,020.00**

Amount to be refunded:

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- a. ☐ A check in the amount of \$_____ to cover the above fees is enclosed.
- b. ☒ Please charge my Deposit Account No. **04-1512** in the amount of \$ **1,020.00** to cover the above fees. A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. **04-1512**. A duplicate copy of this sheet is enclosed.

Note: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

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DATE OF DEPOSIT: **December 14, 2001**

**THIS APPLICATION IS THE ENTRY INTO THE
NATIONAL PHASE UNDER 35 U.S.C. 371**

Applicant(s): Jurgen Schellenberg

International Application No. PCT/DE0001775

International Filing Date: 31 May 2000

Priority Date Claimed: 02 July 1999

**Title: CATALYST COMPOSITION AND PROCEDURE FOR THE MANUFACTURE OF SYNDIOTACTIC
STYRENE POLYMERS**

Attorney's Docket No.: 60843

CATALYST COMPOSITION AND PROCEDURE FOR THE MANUFACTURE OF SYNDIOTACTIC STYRENE POLYMERS

The invention concerns a catalyst composition for the manufacture of syndiotactic styrene polymers, based on fluorine-containing metal complex compounds and a procedure to manufacture these catalyst compositions.

The invention furthermore concerns a procedure for the manufacture of syndiotactic styrene polymers using these catalyst compositions for the preparation of molded articles, for instance by extrusion, injection molding or thermoforming, both in non-reinforced and in fiber-reinforced form.

The complex-coordinative polymerization of styrene monomers to selectively syndiotactic styrene homo and copolymers is accomplished using specific catalyst systems based on metallocenes and their half-sandwich analogs.

Various catalysts or catalyst systems are known for the manufacture of syndiotactic styrene polymers using catalyst compositions based on fluorine-containing metal complex compounds.

In this regard, a catalyst for the polymerization of vinyl-aromatic monomers is known that comprises the reaction product of a η^5 -cyclopentadienyl complex of titanium and an organic-oxidized aluminum compound (EP 0 861 853). This catalyst has the disadvantages, however, that while it leads to syndiotactic polymerization in the mass polymerization of styrene, it requires on the one hand comparatively high concentrations of organic-oxidized aluminum compound, relative to the η^5 -cyclopentadienyl complex of titanium, and on the other, delivers only a relatively small yield in syndiotactic polystyrene and hence shows only low polymerization activity, relative to the catalyst and monomer amounts used and to the polymerization time.

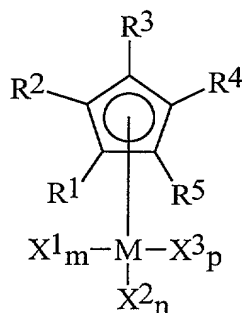
Finally, a catalyst system is known that besides a specific catalyst component contains an organic boron compound, an organo-aluminum compound or an organo-tin compound and is suitable for the polymerization of olefins and the synthesis of syndiotactic polystyrene (WO 97/07141). While higher polymerization activities can be

achieved with this catalyst system, it is still disadvantageous that under the conditions of industrially relevant polymerization procedures, such as mass polymerization, very high molecular weight syndiotactic polystyrenes are obtained, that can hardly be processed with the procedures usual with plastics, such as injection molding or extrusion.

It is hence the task of the invention to develop a catalyst composition for the manufacture of syndiotactic styrene polymers based on fluorine-containing metal complexes, as well as a procedure for the manufacture of syndiotactic styrene polymers using this catalyst composition, that does not show these disadvantages and is characterized by high polymerization activity of the catalyst composition and at the same time, by a reasonable molecular weight of the syndiotactic polystyrenes.

According to the invention, the catalyst composition for the manufacture of syndiotactic styrene polymers based on fluorine-containing metal complexes contains

a) at least one metal complex compound of general formula (I)



(I)

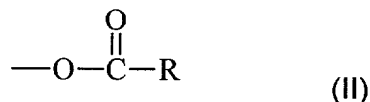
where

M is a metal of subgroup IV or of the lanthanides in the periodic system of elements,

$\text{R}^1, \text{R}^2, \text{R}^3, \text{R}^4, \text{R}^5$ are the same or different and are a hydrogen atom, an alkyl group, an alkenyl group, an aryl group, an aralkyl group, an alkylaryl group, an arylalkenyl group, or a group of structure -OR, -

X^1, X^2, X^3

NR_2 , $-PR_2$, $-SR$ or $-BR_3$ with R equal to or different from R^1 to R^5 , with a number of C atoms per rest of 1 to 25, where one or several rests R^1 to R^5 can form one or more ring systems, are hydrogen, chlorine, an alkyl group, an alkenyl group, an aryl group, an aralkyl group, an alkylaryl group, an alkoxy group, an aryloxy group, an aryloxy group with a number of C atoms per rest of 1 to 15 and at least one group of general formula (II)



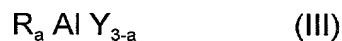
with

R an alkyl group, alkenyl group, aryl group, aralkyl group, alkylaryl group, alkoxy group, aryloxy group with a number of C atoms per rest of 1 to 15, where the rest of the groups X^1 , X^2 and X^3 can be the same or different, and at least one group of formula (II) in addition contains at least one fluorine atom, instead of a hydrogen atom, connected to a C atom, and

m, n, p can be 0, 1, 2 or 3 and the sum of m, n and p is equal 1, 2 or 3,

and which can also be present in dimeric form,

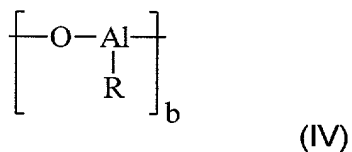
b) at least one organo-aluminum compound of general formula (III)



with

- R being an alkyl group, cycloalkyl group, aryl group, alkyl-aryl group, aralkyl group or alkenyl group with a number of C atoms per rest of 2 to 12,
- Y is hydrogen, halogen or an alkoxy group,
- a is an integer from 1 to 3 and

c) at least one alumoxan of generalized structural formula (IV)



where

- R can be the same or different alkyl groups, aryl groups, arylalkyl groups, alkylaryl groups, alkoxy groups or aryloxy groups with a number of C atoms per rest of 1 to 10, where one or several hydrogen atoms can be substituted by fluorine atoms, and
- b is an integer from 2 to 30.

According to the invention, the molar ratio of organo-aluminum compound to metal complex compounds lies in the range of 0.5 to 300 and the molar ratio of alumoxanes to the metal complex compounds is of 5 to 1000.

According to the invention, the metal complex compound contains, as η^5 -cyclopentadienyl group coordinated to the metal, the pentamethyl-cyclopentadienyl group, the indenyl group, the tetrahydro-indenyl group, the fluorenyl group or the tetrahydro-fluorenyl group.

According to the invention, the metal complex compound contains the octahydro-fluorenyl group as η^5 -cyclopentadienyl group coordinated to the metal.

According to the invention, the catalyst composition contains, as group of general formula (II) of the metal complex compounds, the trifluoro-acetate group or/and the pentafluoro-benzoate group.

According to the invention, the organo-aluminum compound of general formula (III) of the catalyst composition used is one in which a has a value of 3. Tri-isobutyl-aluminum can be used as organo-aluminum compound of general formula (III).

According to the invention, the alumoxan of generalized structural formula (IV) of the catalyst composition can be partially or complete substituted by one or more organic boron compounds.

The alumoxan of generalized structural formula (IV) used can be a methyl-alumoxan.

According to the invention, the manufacture of the catalyst composition can be accomplished by reacting the components mentioned in reverse order.

According to the invention, the catalyst composition mentioned is used for the manufacture of polymers and copolymers, in particular of syndiotactic styrene polymers.

According to the invention, the syndiotactic styrene polymers can be manufactured by polymerizing the monomers in the presence of the catalyst compositions mentioned, at a molar ratio of monomers to metal complex compounds of general formula (I) of 20 to 1,000,000, preferably of 30,000 to 800,000 and at temperatures of 20 °C to 130 °C, preferably of 40 °C to 100 °C.

Styrene can be used as monomer for the manufacture of syndiotactic styrene polymers, according to the invention. Furthermore, substituted styrenes can be used as monomers. Other vinyl monomers can also be used as comonomers. Thus, styrene and p-methyl-styrene can be used as monomers.

According to the invention, substances acting as donors towards the metal complex compounds can additionally be included, during the manufacture of syndiotactic styrene polymers. Examples of such substances acting as donors are, for instance, phenyl-silane or octyl-silane.

Finally, according to the invention syndiotactic styrene polymers can be manufactured by polymerization with the catalyst composition mentioned.

The invention will be further elucidated below by means of some selected implementation examples.

Example 1:

Manufacture of η^5 -pentamethyl-cyclopentadienyl-titanium-bis-(trifluoro-acetate) as dimer

The starting point for the manufacture of η^5 -pentamethyl-cyclopentadienyl-titanium-bis-(trifluoro-acetate) as dimer was η^5 -1, 2, 3, 4, 5-pentamethyl-cyclopentadienyl-titanium-trimethanolate as intermediate compound. To this end, 3.33 ml of a 0.5 molar solution of this compound in toluene were added slowly, with stirring, at room temperature, in 10 ml of a 1 molar solution of trifluoro-acetic acid in toluene, in a glove box under argon atmosphere and then left for another 20 hours under these conditions. Next the solvent was partially removed at reduced pressure and the η^5 -pentamethyl-cyclopentadienyl-titanium-bis-(trifluoro-acetate) was crystallized out as the dimer. Still inside the glove box the crystals were separated and washed with a little toluene. After drying they had an intensely brownish-red color.

The elementary analysis of the end product yielded the following values:

$[(Cp^*Ti(OCOCF_3)_2)_2]$:

Experimental: C: 41.8 % H: 3.9 % Ti: 11.5 %

Calculated: C: 41.0 % H: 3.9 % Ti: 11.7 %

Polymerization with this metal complex compound:

For the polymerization of styrene to a syndiotactic polymer a catalyst premix was prepared as a solution in a 10 ml measuring cylinder by the sequential addition of 3.73 ml of a 1.61 molar methyl-alumoxan solution in toluene, 3 ml of a 1.0 molar triisobutyl-aluminum solution in toluene, 3.0 ml of a 0.0127 molar solution of η^5 -pentamethyl-cyclopentadienyl-titanium-bis-(trifluoro-acetate) (calculated as monomer) in toluene and the residual amount in toluene, in a glove box under argon atmosphere, with stirring, leaving it to condition for 45 min.

To perform the polymerizations, glass ampoules with a curved bottom, also in a glove box under argon atmosphere, were each filled with 5 ml styrene and sealed with septa and a flared aluminum joint. The styrene had been previously purified by eliminating oxygen by washing with nitrogen, passing over an activated aluminum oxide column and hydrogenation using a palladium catalyst to remove phenylacetylene. After transferring the catalyst premix and the styrene ampoules out of the glove box, the latter were temperature-conditioned in a water bath, to polymerization temperature, for 10 min. Polymerization was started by the inert addition of 63 μ l of the premix solution under intense homogenization. The chosen polymerization temperature was 50 °C and the polymerization time, 45 min. After the chosen reaction time, polymerization was stopped by addition of methanol. The polymer obtained was separated and dried in a vacuum for 40 min at 150 °C and 30 min at 250 °C. The polymerization yield was determined based on the weighings. The molar ratios of the components in the composition was, in this case: styrene : MAO : TIBA : Ti = 233,333 : 200 : 100 : 1.27.

The result found was a polymerization conversion of 27.9 wt.-% and from it, the polymerization activity of the catalyst composition, in kg syndiotactic polystyrene, relative to the amount of metal complex compound (as monomer) in mol, the amount of styrene in mol and the polymerization time in h, as 48,500. The melting temperature (T_m) was determined using DSC, as 268 °C and the crystallization temperature (T_k) as 216 °C.

Example 2: (Comparison example)

In this example the same metal complex compound as in Example 1, η^5 -pentamethyl-cyclopentadienyl-titanium-bis-(trifluoro-acetate) was used, as dimer, and processed under polymerization conditions similar to those in Example 1, except that tri-isobutyl-aluminum was not used, as organo-aluminum compound of general formula $R_a Al Y_{3-a}$. A polymerization conversion of 11.9 wt.-% was determined and from

it, a polymerization activity of the catalyst composition of 20,600 kg SPS/(mol cat x mol St x h).

As these polymerization results for the syndiotactic polystyrene obtained document, in comparison to those of Example 1, in this procedure that is not according to the invention, in particular much lower polymerization conversion rates and hence, strongly reduced polymerization activities, are obtained.

Example 3:

Manufacture of η^5 -octahydro-fluorenyl-titanium-dimethoxy-monotrifluoroacetate

For the preparation of η^5 -octahydro-fluorenyl-titanium-dimethoxy-monotrifluoroacetate, η^5 -1, 2, 3, 4, 5, 6, 7, 8-octahydro-fluorenyl-titanium-trimethanolate was chosen as starting compound. In a glove box and under argon atmosphere, 10 ml of a 1.0 molar solution of this starting compound in toluene were slowly combined with 10 ml of a 1.0 molar solution of trifluoro-acetic acid in toluene at 25 °C, with stirring and left for another 20 hours of after-reaction. This mixture was then carefully concentrated, with stirring and at reduced pressure and then left for several days in this manner. Finally all volatile components were removed in a high vacuum. A more highly viscous liquid of yellow-orange color was obtained.

The elementary analysis of the end product yielded the following values:

Experimental: C: 52.6 % H: 6.0 % Ti: 12.8 %

Calculated: C: 51.5 % H: 5.9 % Ti: 12.1 %

Polymerization with this metal complex compound:

The realization of the polymerizations with this metal complex compound as component of the catalyst composition was accomplished under the same preparation, polymerization and processing conditions as in Example 1, except that a 0.01 molar solution of the metal complex compound was used to prepare the premix and therefore, the molar ratios of the components in the composition were styrene : MAO : TIBA: Ti = 233,333 : 200 : 100 : 1. The conversion rate obtained and the polymeriza-

tion activity calculated therefrom, as well as the characteristic values of the syndiotactic polystyrene obtained, including the weight average molecular weights M_w in g/mol obtained based on molecular weights defined by means of SEC by calibration with normal polystyrenes and the polydispersity as ratio of weight average and number average molecular weights, are shown in Table 1.

Example 4

Manufacture of η^5 -octahydro-fluorenyl-titanium-tris-(pentafluoro-benzoate)

The compound η^5 -1, 2, 3, 4, 5, 6, 7, 8-octahydro-fluorenyl-titanium-trimethanolate was also the starting material for the preparation of η^5 -octahydro-fluorenyl-titanium-tris-(pentafluoro-benzoate). 4 ml of a 0.5 molar solution of this compound in toluene as solvent were added slowly to 12 ml of a 0.5 molar solution of pentafluoro-benzoic acid in toluene, at room temperature, under argon atmosphere, in a glove box, with stirring and left for another 20 hours at room temperature. Subsequently this mixture was carefully concentrated at reduced pressure, with stirring and left in this manner for several days. The product was then separated inside the glove box, picked up several times in toluene and the volatile components were completely removed in a high vacuum. The product obtained was of dark reddish brown color.

The elementary analysis of the end product yielded the following values:

Experimental:	C: 48.5 %	H: 2.1 %	Ti: 5.9 %
Calculated:	C: 47.8 %	H: 2.0 %	Ti: 5.6 %

Polymerization with this metal complex compound:

Also with this metal complex compound as component of the catalyst composition, the investigation of the polymerization behavior proceeded as in the preparation, polymerization and processing conditions indicated in Example 3; the polymerization conversion rate and the polymerization activity determined from it, and the properties of the syndiotactic polystyrene are shown in Table 1.

Example 5 (comparison example)

In analogy to Example 4, η^5 -octahydro-fluorenyl-titanium-tris-(pentafluoro-benzoate) was used as metal complex compound and processed under the polymerization conditions of Example 4, except that no tri-isobutyl-aluminum was used as organo-aluminum compound of general formula $R_a Al Y_{3-a}$.

The polymerization result, also shown in Table 1 and the properties of the syndiotactic polystyrene manufactured show, in comparison to those of Example 4, that the consequences of this procedure not according to the invention are a substantially smaller polymerization conversion rate and hence, a strongly reduced polymerization activity.

Examples 6 through 10

Examples 6 through 10 were obtained using the metal complex compounds manufactured in Examples 1, 3 and 4 with the catalyst compositions prepared according to Example 1 (Example 8), or Example 3 (Examples 6, 7, 9 and 10), according to the polymerization and processing conditions of Example 1 (Example 8) or Example 3 (Examples 6, 7, 9 and 10). Processing was similar to the indications in Table 2, with the corresponding metal complex compounds, at polymerization temperatures of 50 °C or 70 °C and polymerization times of 15 min. At the same time, Table 2 provides an overview of conversion rates and properties of the polymerides and thus documents the very high polymerization activities of the catalyst compositions according to the invention, as well as the excellent properties of polymerides obtainable according to the invention.

Example 11 (Comparison example)

In this Example, η^5 -pentamethyl-cyclopentadienyl-titanium-trifluoride is used as metal complex compound in the catalyst composition; processing is according to the procedure of Example 6. The analysis of the syndiotactic polystyrene obtained by means of SEC yielded a weight average molecular weight M_w of 1,530,000 g/mol with a polydispersity expressed as ratio of the weight average and the numerical average molecular weight, of 3.3.

Such a polymeride, obtained under conditions comparable to those of the above examples according to the invention, has such an extremely high weight average molecular weight M_w , that suitable processing of these syndiotactic polystyrenes under the processing procedures and conditions customary for plastic, such as injection molding or extrusion, is not possible.

Table 1 Polymerization results and properties of the syndiotactic polystyrenes of Examples 3 through 5

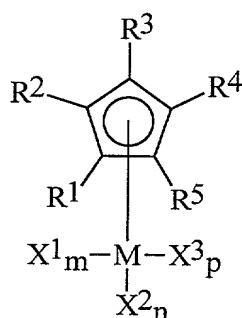
Example Nor.	Metal complex compound	Polymerization temperature [°C]	Polymerization time [min]	Conversion [wt.-%]	Polymerization activity [kg SPS/(mol cat x mol St x h)]x10 ⁻³	M _w [g/mol]x10 ⁻³	Polydispersity	T _m [°C]	T _k [°C]
3	[656]Ti(OMe) ₂ -(OCOCF ₃)	50	45	46.3	102.2	781	2.1	270	214
4	[656]Ti(OCOCF ₅) ₃	50	45	59.9	131.8	787	2.2	270	219
5	[656]Ti(OCOCF ₅) ₃	50	45	2.1	4.6	-	-	-	-

Table 2 Polymerization results and properties of the syndiotactic polystyrenes of Examples 6 through 10

Example No.	Metal complex compound	Polymerization temperature [°C]	Polymerization time [min]	Conversion-%	Polymerization activity [kg SPS/(mol cat x mol St x h)] x 10 ⁻³	M _w [g/mol] x 10 ⁻³	Polydispersity	T _m [°C]	T _k [°C]
6	[656]Ti(OMe) ₂ -(OCOCF ₃)	50	15	12.4	82.0	1120	2.8	270	217
7	[656]Ti(OCOCF ₃) ₃	50	15	24.1	159.5	1220	2.5	270	217
8	(Cp ⁺ Ti(OCOCF ₃) ₂) ₂	70	15	25.3	132.0	1250	2.5	268	214
9	[656]Ti(OMe) ₂ -(OCOCF ₃)	70	15	45.2	299.5	376	2.0	270	220
10	[656]Ti(OCOCF ₃) ₃	70	15	55.2	365.4	396	2.2	270	222

Patent claims

1. Catalyst composition for the manufacture of syndiotactic styrene polymers based on fluorine-containing metal complex compounds that include
 - a) at least one metal complex compound of general formula (I)



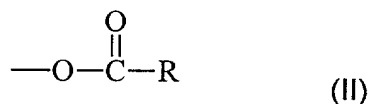
(I)

where

M is a metal of subgroup IV or of the lanthanides, in the periodic system of elements, preferably Ti;

R¹, R², R³, R⁴, R⁵ are the same or different and are a hydrogen atom, an alkyl group, alkenyl group, aryl group, aralkyl group, alkylaryl group, arylalkenyl group, or a group with the structure -OR, -NR₂, -PR₂, -SR or -BR₃ with R equal to or different, analogous to R¹ to R⁵ with the number of C atoms per rest of 1 to 25, where one or several rests R¹ to R⁵ can together form one or several ring systems,

X¹, X², X³ are hydrogen, chlorine, an alkyl group, alkenyl group, aryl group, aralkyl group, alkylaryl group, alkoxy group, aryloxy group with a number of C atoms per rest of 1 to 15 and at least one group of general formula (II)



with

R an alkyl group, alkenyl group, aryl group, aralkyl group, alkylaryl group, alkoxy group, aryloxy group with a number of C atoms per rest of 1 to 15, where the remainder of the groups X¹, X² and X³ can be the same or different and represents at least one group of formula (II) and in addition, contains at least one fluorine

atom instead of a hydrogen atom on a carbon and

m, n, p can be 0, 1, 2 or 3 and the sum of m, n and p equals 1, 2 or 3, and which can also be present in dimeric form.

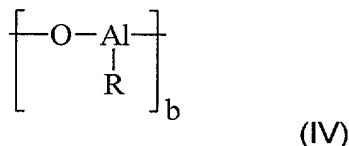
b) at least one organo-aluminum compound of general formula (III)



with

R an alkyl group, cycloalkyl group, aryl group, alkylaryl group, aralkyl group or alkenyl group with a number of C atoms per rest of 2 to 12,
 Y a hydrogen, halogen or alkoxy group,
 a an integer between 1 and 3 and

c) at least one alumoxane of general structural formula (IV)



where

R can be the same or different alkyl groups, aryl groups, aralkyl groups, alkylaryl groups, alkoxy groups or aryloxy groups with a number of C atoms per rest of 1 to 10, where one or several hydrogen atoms can be substituted by fluorine atoms, and
 b is an integer from 2 to 30.

2. Catalyst composition according to claim 1, **characterized by** the molar ratio of organo-aluminum compound to metal complex compound being in the range of 0.5 to 300.
3. Catalyst composition according to claims 1 and 2, **characterized by** the molar ratio of alumoxanes to metal complex compounds being of 5 to 1000.
4. Catalyst composition according to claims 1 through 3, containing as η^5 -cyclopentadienyl group of the metal complex compound coordinated to the metal, the cyclopentadienyl group, the pentamethyl-cyclopentadienyl group, the indenyl group, the tetrahydro-indenyl group, the fluorenyl group or the tetrahydro-fluorenyl group.
5. Catalyst composition according to claims 1 through 3, containing as η^5 -cyclopentadienyl group of the metal complex compound coordinated to the metal, the octahydro-fluorenyl group.

6. Catalyst composition according to claims 1 through 5, containing as group of general formula (II) of the metal complex compound, the trifluoro-acetate group.
7. Catalyst composition according to claims 1 through 5, containing as group of general formula (II) of the metal complex compound, the pentafluoro-benzoate group.
8. Catalyst composition according to claims 1 through 7, **characterized by** the organo-aluminum compound of general formula (III) being one in which a has a value of 3.
9. Catalyst composition according to claims 1 through 8, **characterized by** the organo-aluminum compound of general formula (III) used being tri-isobutyl-aluminum.
10. Catalyst composition according to claims 1 through 9, **characterized by** the alumoxane of generalized structural formula (IV) being partially or entirely substituted by one or several organic boron compounds.
11. Catalyst composition according to claims 1 through 10, **characterized by** using, as alumoxane of generalized structural formula (IV), a methyl-alumoxane.
12. Procedure for the manufacture of the catalyst composition mentioned in claim 1, **characterized by** the reaction of the components mentioned in claim 1 taking place in reversed order.
13. Utilization of the catalyst composition mentioned in claim 1 for the manufacture of polymers and copolymers, in particular of syndiotactic styrene polymers.
14. Procedure for the manufacture of syndiotactic styrene polymers, **characterized by** the monomers being polymerized in the presence of the catalyst composition mentioned in claim 1 at a molar ratio of monomers to metal complex compounds of general formula (I) of 20 to 1,000,000, preferably of 30,000 to 800,000 and at temperatures of 20 °C to 130 °C, preferably of 40 °C to 100 °C.
15. Procedure for the manufacture of syndiotactic styrene polymers according to claim 14, **characterized by** using styrene as monomer.
16. Procedure for the manufacture of syndiotactic styrene polymers according to claims 14 and 15, **characterized by** using substituted styrenes as monomers.
17. Procedure for the manufacture of syndiotactic styrene polymers according to claims 14 through 16, **characterized by** using other vinyl monomers as comonomers.

18. Procedure for the manufacture of syndiotactic styrene polymers according to claims 14 through 16, **characterized by** using styrene and p-methyl-styrene as monomers.
19. Procedure for the manufacture of syndiotactic styrene polymers according to claims 14 through 18, **characterized by** additionally using substances that act as donors towards the metal complex compounds.
20. Procedure for the manufacture of syndiotactic styrene polymers according to claims 14 through 19, **characterized by** the substances acting as donors being phenyl-silane or octyl-silane.

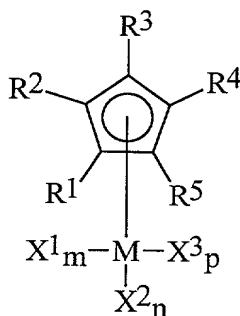
Summary

Catalyst composition and procedure for the manufacture of syndiotactic styrene polymers

The invention concerns a catalyst composition for the manufacture of syndiotactic styrene polymers based on fluorine-containing metal complex compounds, a procedure for the manufacture of these catalyst compositions and a procedure for the manufacture of syndiotactic styrene polymers using this catalyst composition for the preparation of molded articles, for instance by extrusion, injection molding or thermoforming, both in non-reinforced and in fiber-reinforced form.

According to the invention, the catalyst composition for the manufacture of syndiotactic styrene polymers based on fluorine-containing metal complex compounds contains

- a) at least one metal complex compound of general formula



and

- b) at least one organo-aluminum compound

and

- c) at least one alumoxane.

This Assignment 1000 is in the ENGLISH language and has the same meaning in other languages with the same 1000 number and R/Date

USA/PCT

(a) My residence and Citizenship are as stated below my name. My P.O. (mailing) address is the same as my residence unless otherwise stated.
(b) I verily believe I am/we are the original, first and sole/joint inventor(s) of the subject matter that is embraced by and for which a patent is sought on the invention entitled: **CATALYST COMPOSITION AND PROCEDURE FOR THE MANUFACTURE OF SYNDIOTACTIC STYRENE POLYMERS**

☒ was filed on May 31, 2000 as (60843).
Application No. PCT/DE0001775
and was amended on

- (c) I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.
- (d) I acknowledge my duty under 37 CFR 1.56 to disclose to the U.S. Patent and Trademark Office all information known to me to be material to patentability as defined in 37 CFR 1.56(b). If this application is a continuation-in-part application, I acknowledge the duty to disclose all information known to me to be material to patentability as defined in 37 CFR 1.56(b) that became available between the filing date of the prior application from which priority is claimed in part (f) below, and the national or PCT international filing date of this application.
- (e) I hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate listed below or §365(a) of any PCT international application that designated at least one country other than the United States of America listed below, and also identify below any other foreign equivalent application for patent or inventor's certificate or any other equivalent PCT international application having a filing date before that of the application on which priority is claimed:
Additional claims for benefit are attached.

I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith. Address all correspondence to The Dow Chemical Company's appointed counsel at:



I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both under 18 U.S.C. § 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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P. O. Address: Same as Residence

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Citizenship: _____
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At: _____
this _____ day of _____ 20____

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